1998-05-01

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Journal Name: Journal of Chemical Physics; Journal Volume: 108; Journal Issue: 17;
Other Information: PBD: May 1998
http://hdl.handle.net/10945/61041

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Cite as: J. Chem. Phys. **108**, 7266 (1998); https://doi.org/10.1063/1.476144
Submitted: 03 September 1997 . Accepted: 30 January 1998 . Published Online: 04 June 1998

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Classical Heisenberg model of magnetic molecular ring clusters: Accurate approximants for correlation functions and susceptibility

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(Received 3 September 1997; accepted 30 January 1998)

We show that the measured magnetic susceptibility of molecular ring clusters can be accurately reproduced, for all but low temperatures T, by a classical Heisenberg model of N identical spins S on a ring that interact with isotropic nearest-neighbor interactions. While exact expressions for the two-spin correlation function, $C_N(n,T)$, and the zero-field magnetic susceptibility, $\chi_N(T)$, are known for the classical Heisenberg ring, their evaluation involves summing infinite series of modified spherical Bessel functions. By contrast, the formula $C_N(n,T)=(u^n+u^{N-n})/(1+u^N)$, where $u(K)=\coth K-K^{-1}$ is the Langevin function and $K=JS(S+1)/(k_BT)$ is the nearest-neighbor dimensionless coupling constant, provides an excellent approximation if $N\geqslant 6$ for the regime $|K|<3$. This choice of approximant combines the expected exponential decay of correlations for increasing yet small values of n, with the cyclic boundary condition for a finite ring, $C_N(n,T)=C_N(N-n,T)$. By way of illustration, we show that, for $T>50$ K, the associated approximant for the susceptibility derived from the approximate correlation function is virtually indistinguishable from both the exact theoretical susceptibility and the experimental data for the ''ferric wheel'' molecular cluster ($[Fe(OCH_3)_2(O_2CCH_2Cl)]_{10}$), which contains $N=10$ interacting Fe^{3+} ions, each of spin $S=5/2$, that are symmetrically positioned in a nearly planar ring. © *1998 American Institute of Physics.* [S0021-9606(98)02317-4]

I. INTRODUCTION

Recent advances in the fabrication of molecular magnets portend an unprecedented ability to control the placement of magnetic moments in molecular structures and hence to design and produce nanometer-scale magnetic systems.[1,2] A wide variety of molecular clusters containing relatively small numbers of magnetic ions (e.g., as few as four) can now be fabricated[3,4] and these provide novel systems in which to test basic theories of magnetism and offer the prospect of new applications. Quite often the magnetic moments are symmetrically positioned in a simple ring structure within the host cluster, as in the ''ferric wheel'' molecule,[4] where each cluster contains ten Fe^{3+} ions of spin $S=5/2$ that define a nearly planar ring. Ring-shaped magnetic nanostructures thus provide a new class of materials in which to test one-dimensional models of magnetism.[5] Materials containing very long chains of magnetic atoms, such as TMMC, have of course long been known.[6] Ring nanomagnets, however, are sufficiently small that the effects of the cyclic geometry can manifest in the experimentally observed magnetic properties. In applying ''one-dimensional'' models, therefore, one must distinguish theoretical results in which cyclic boundary conditions are employed from those for open chains.[7] Only for sufficiently large systems, of course, does the nature of the boundary condition become immaterial. For the above-mentioned ferric-wheel system, it has been remarked[4] that a quantum-mechanical determination of the allowed energy levels of this ring of ten interacting $S=5/2$ spins exceeds the capability of present-day computers. This clearly underscores the need for simplified yet realistic ''mesoscopic'' models of ring nanomagnets. Furthermore, it is important to establish the lowest temperature, for given spin S, that a classical treatment of interacting spins suffices.

The purpose of this article is twofold. We show, except for low temperatures where quantum effects dominate, that an approximate, *classical* treatment of interacting Heisenberg spins can provide results for the magnetic susceptibility of small ring structures in excellent agreement with experiment. We illustrate this explicitly with susceptibility data[8] from the ferric wheel molecular cluster; we have, however, also analyzed susceptibility data from several other ring molecular clusters and likewise find close agreement between experiment and the classical theory for all but low temperatures.[9] The second purpose of this article is to present simple analytic approximants for the two-spin correlation function, $C_N(n,T)=\langle \hat{e}_i\cdot\hat{e}_{i+n}\rangle_N$, and the zero-field magnetic susceptibility, $\chi_N(T)$, for a ring of N classical Heisenberg spins that are valid for all but low temperatures. (As explained in Sec. II A, a classical spin at site i is described by a unit vector, $\hat{e}_i$, free to point in any direction.) While exact expressions for these quantities have been derived,[10] evaluating these expressions entails the summation of infinite series of modified spherical Bessel functions. These series are such that, for progressively lower temperatures, increasingly more terms must be included in the sum

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to achieve good accuracy. Besides the tedium of summing large numbers of modified spherical Bessel functions, computing these functions in the large-argument, large-order regime will usually trigger numerical instabilities unless specific countermeasures are employed.[11] By contrast, for the associated *open* chain of classical Heisenberg spins, the expressions for the correlation function and susceptibility are extremely simple.[12] Physically motivated, *approximate* expressions for these quantities for the ring, of comparable simplicity with those for the open chain, would therefore be highly desirable.

We find that the formula $C_N(n,T)=[\nu^n(N,K)+\nu^{N-n}(N,K)]/[1+\nu^N(N,K)]$ provides an *excellent* approximation for the correlation function, where $\nu(N,K)$ is an appropriately chosen function and $K=JS(S+1)/(k_BT)$ is the dimensionless nearest-neighbor coupling constant. Note that this approximant: First, incorporates exponential decay of correlations, which is to be expected for small, increasing values of n; second, satisfies the cyclic boundary condition for the correlation function associated with a finite ring, $C_N(n,T)=C_N(N-n,T)$; and, third, satisfies the requirement that $C_N(0,T)=1$, which follows from the fact that $\hat{e}_i$ is a unit vector. We note that if $n\ll N$, the values of $C_N(n,T)$ for a ring should differ negligibly from that for an open chain, for which the correlation function is given by[12] $C_N^{\text{chain}}(n,K)=u^n(K)$, independent of N, where $u(K)\equiv\coth K-K^{-1}$ denotes the Langevin function. Now, for $n\ll N$, our approximant is essentially given by $\nu^n(N,K)$, suggesting that if $N\gg 1$ we have $\nu(N,K)\approx u(K)$. This leads to our simplest, least accurate choice, $\nu(N,K)=u(K)$ for all values of N. [A procedure for selecting more accurate forms of $\nu(N,K)$ is given in Sec. III.] Even for this simplest choice, however, i.e., $\nu(N,K)=u(K)$, we find that the resulting approximant provides excellent results for $|K|<3$ as long as $N\geqslant 6$. We also find that the associated result for the zero-field susceptibility, $\chi_N(T)$, derived from the approximate correlation function, is in excellent numerical agreement with both the exact susceptibility, and, for $T>50$ K, with experimental data for the molecular ferric wheel. We note that below approximately 40 K this system cannot be accurately described by the classical Heisenberg model. Thus, in comparing with experiment, there is no advantage gained in utilizing the exact susceptibility of the classical Heisenberg model rather than the much simpler approximate formula [see Eq. (3.5)] which is based on the above choice, $\nu(N,K)=u(K)$. Elsewhere,[13] we provide estimates for the lowest temperature for which results derived using the classical Heisenberg model can accurately approximate a ring of N spins S described by the quantum Heisenberg model.

This article is organized as follows. In the next section we briefly review some of the exact thermodynamic properties of classical Heisenberg rings. In Sec. III we present our approximants for the correlation function and magnetic susceptibility. The predictions of these approximants are then compared to exact results. Finally, in Sec. IV we compare our results for the susceptibility with experimental data for the molecular ferric wheel. It is our hope that the present work will simplify the analytical treatment of small Heisenberg rings and thus aid both in understanding and developing nanomagnets.

II. EXACT RESULTS

A. Classical Heisenberg model

To fix the notation, the quantum Heisenberg model of N identical spins on a ring with isotropic nearest-neighbor interactions is written as

$$H=-J\sum_{i=1}^{N}\mathbf{S}_i\cdot\mathbf{S}_{i+1}-\mu\mathbf{B}\cdot\sum_{i=1}^{N}\mathbf{S}_i. \tag{2.1}$$

The $\mathbf{S}_i$ are quantum spin operators in units of $\hbar$, with $\mathbf{S}_{N+1}\equiv\mathbf{S}_1$, J is the exchange interaction energy, $\mathbf{B}$ is the external magnetic field, and $\mu=-g\mu_B$, with g the Landé g factor and μ_B the Bohr magneton. We note that $(J<0)$ $J>0$ promotes (anti-) ferromagnetic ordering at low temperatures. We will explore the properties of the classical counterpart of Eq. (2.1) obtained by replacing the quantum spin operators with classical vectors of length $\sqrt{S(S+1)}$ that are free to point in any direction. Rescaling J by $J\to J_c\equiv S(S+1)J$ and μ by $\mu\to\mu_c\equiv\mu\sqrt{S(S+1)}$ results in the $n=3$ version of the n-vector model for spins on a ring,

$$H_c=-J_c\sum_{i=1}^{N}\hat{e}_i\cdot\hat{e}_{i+1}-\mu_c\mathbf{B}\cdot\sum_{i=1}^{N}\hat{e}_i, \tag{2.1$'$}$$

where $\hat{e}_{N+1}\equiv\hat{e}_1$. In what follows we consider $B=0$.

B. Correlation functions

The two-spin correlation function for the N-spin ring is given by

$$C_N(n,T)=\langle\hat{e}_i\cdot\hat{e}_{i+n}\rangle_N\equiv Z_N^{-1}\int d\Gamma\ \exp(-\beta H_c)\hat{e}_i\cdot\hat{e}_{i+n}, \tag{2.2}$$

where $\beta\equiv(k_BT)^{-1}$, $d\Gamma\equiv\Pi_{i=1}^{N}(d\Omega_i/4\pi)$, with $d\Omega_i=\sin\theta_i\,d\theta_i\,d\phi_i$ the element of solid angle about $\hat{e}_i$, and where Z_N is the partition function, $Z_N=\int d\Gamma\ \exp(-\beta H_c)$. For a finite ring with translational symmetry, the correlation function must satisfy the cyclic property,

$$C_N(n,T)=C_N(N-n,T). \tag{2.3}$$

For zero magnetic field, Joyce[10] has derived an expression for the correlation function as a double infinite series involving modified spherical Bessel functions and the Wigner $3j$-symbol,

$$C_N(n,K)=Z_N^{-1}\sum_{l_1=0}^{\infty}\sum_{l_2=0}^{\infty}(2l_1+1)(2l_2+1)\times f_{l_1}^{n}(K)f_{l_2}^{N-n}(K)\begin{pmatrix}l_1 & l_2 & 1\\ 0 & 0 & 0\end{pmatrix}^2, \tag{2.4}$$

where $f_l(K)\equiv\sqrt{\pi/(2K)}I_{l+(1/2)}(K)$ is the modified spherical Bessel function of order l. The functions $f_l(K)$ decay extremely rapidly with increasing l for $l>|K|$. Thus for numerical calculations, the higher the temperature, the fewer

the terms of Eq. (2.4) that are required to be summed. Joyce has also shown[10] that for zero magnetic field the partition function may be written as an infinite series

$$Z_N(K)=\sum_{l=0}^{\infty}(2l+1)f_l^N(K). \tag{2.5}$$

We now simplify Eq. (2.4) as well as derive a number of useful new results. We first show that Eq. (2.4) can be written in such a form as to manifestly satisfy Eq. (2.3). The only[14] nonzero $3j$-symbols of the type appearing in Eq. (2.4) are given by[15]

$$\begin{pmatrix} a & a+1 & 1 \\ 0 & 0 & 0 \end{pmatrix}^2=\begin{pmatrix} a+1 & a & 1 \\ 0 & 0 & 0 \end{pmatrix}^2 =\frac{a+1}{(2a+1)(2a+3)}, \tag{2.6}$$

where a is an integer. Using Eq. (2.6), the double sum in Eq. (2.4) reduces to a single infinite sum and one obtains

$$C_N(n,K)=Z_N^{-1}\sum_{l=0}^{\infty}(l+1)f_l^N(K)[\rho_l^n(K)+\rho_l^{N-n}(K)], \tag{2.7}$$

where $\rho_l(K)\equiv f_{l+1}(K)/f_l(K)$. It thus follows at once from Eq. (2.7) that the cyclic property Eq. (2.3) is obeyed. It will now be useful to obtain the $N\to\infty$ limit of Eq. (2.7), for fixed values of n. By first dividing out f_0^N from the two infinite series appearing in Eq. (2.7), which includes Z_N as given by Eq. (2.5), and using the property that $|\rho_l(K)|<1$, the limit $N\to\infty$ can readily be taken, with the result

$$\lim_{N\to\infty} C_N(n,K)=\rho_0^n(K)\equiv u^n(K), \tag{2.8}$$

where

$$u(K)\equiv I_{3/2}(K)/I_{1/2}(K)=\coth K-K^{-1} \tag{2.9}$$

is the Langevin function. For the *infinite* ring, therefore, the decay of the correlation function is exclusively exponential, with a correlation length ξ given by $\xi^{-1}=-\ln[|\coth K-K^{-1}|]$. In the limit $N\to\infty$, the correlation function should of course be independent of the nature of the boundary conditions. Indeed, the result in this limiting case is consistent with Fisher's finding[12] that for the open chain of classical Heisenberg spins,

$$C_N^{\text{chain}}(n,K)=u^n(K), \tag{2.10}$$

independent of N.

We now list several additional exact results. The functions $f_l(K)$ have the parity property that $f_l(-K)=(-1)^l f_l(K)$ and hence that $\rho_l(-K)=-\rho_l(K)$. It then follows that for a ring with N even, $C_N(n,-K)=(-1)^n C_N(n,K)$. For odd N, however, there is no analogous relation between the correlation functions for ferro- and antiferromagnetic couplings. We also note that the result Eq. (2.7), in the special case $n=0$, can be shown to satisfy the requirement that $C_N(0,K)=1$. Finally, we remark that one can directly obtain analytic expressions in closed form for Z_2, Z_3, $C_2(1)$, and $C_3(1)=C_3(2)$ by starting from Eqs. (2.1′), (2.2), and the definition of the partition function. The results for $N=2$ are $Z_2(K)=\sinh(2K)/(2K)$ and $C_2(1,K)=u(2K)$. Identical results emerge from the series expansions (2.5) and (2.7), respectively, which can be summed for this special value of N. We demonstrate this for Z_2 by utilizing the following special case of the Gegenbauer addition theorem for Bessel functions:[16]

$$\frac{\sin\omega}{\omega}=\frac{\pi}{\sqrt{Zz}}\sum_{l=0}^{\infty}\left(l+\frac{1}{2}\right)J_{l+(1/2)}(Z)J_{l+(1/2)}(z)\times P_l(\cos\phi), \tag{2.11}$$

where $\omega=\sqrt{Z^2+z^2-2Zz\cos\phi}$ and P_l denotes the Legendre polynomial. Selecting $Z=z=iK$ and $\phi=\pi$, and using the fact that $J_{l+(1/2)}(iK)=\exp[i(\pi/2)(l+\frac{1}{2})]I_{l+(1/2)}(K)$ for real K, one readily finds that

$$Z_2(K)=\sum_{l=0}^{\infty}(2l+1)f_l^2(K)=\frac{\sinh(2K)}{2K}, \tag{2.12}$$

as claimed. The expressions for Z_3 and $C_3(1)$ are somewhat lengthy and are given in Ref. 13.

C. Susceptibility

The zero-field susceptibility *per spin* can be written as

$$\chi_N(K)=(\beta\mu_c^2/3)\tilde{\chi}_N(K), \tag{2.13a}$$

where

$$\tilde{\chi}_N(K)\equiv N^{-1}\sum_{i,j=1}^{N}\langle\hat{e}_i\cdot\hat{e}_j\rangle_N. \tag{2.13b}$$

For sufficiently high temperatures, where all the spins are uncorrelated, the quantity $\tilde{\chi}_N$ approaches unity and Eq. (2.13a) reduces to the statement of Curie's law. Using the representation (2.7) of the correlation function, one can readily derive the following expression for $\tilde{\chi}_N(K)$:

$$\tilde{\chi}_N(K)=1+2Z_N^{-1}\sum_{l=0}^{\infty}(l+1)\left[\frac{f_l^N f_{l+1}-f_l f_{l+1}^N}{f_l-f_{l+1}}\right]. \tag{2.14}$$

We now examine several special cases of Eq. (2.14). First, considering the limit $N\to\infty$ in Eq. (2.14), it can be shown that

$$\lim_{N\to\infty}\tilde{\chi}_N(K)=\frac{1+u(K)}{1-u(K)}. \tag{2.15}$$

This form for the susceptibility is common to infinite, one-dimensional models with an exponentially decaying correlation function, where the parameter u can be identified in terms of the correlation length, $|u|=\exp(-\xi^{-1})$. We also note that for the case $N=2$, it can be shown that Eq. (2.14) reduces to the correct expression $\tilde{\chi}_2(K)=1+u(2K)$, which follows directly from Eq. (2.13b). Finally, for $N=1$, Eq. (2.14) reduces to unity and hence we have $\chi_1=\beta\mu_c^2/3$, which is the correct zero-field susceptibility for a single paramagnetic spin.

We note that the susceptibility per spin for the associated N-spin open chain can be obtained by substituting Eq. (2.10) into Eq. (2.13b), with the result

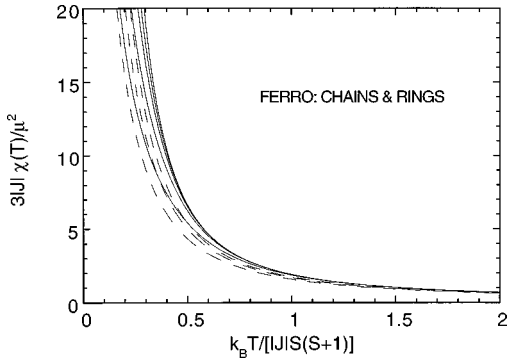

FIG. 1. Zero-field magnetic susceptibility per spin, for rings and chains consisting of N spins interacting with ferromagnetic nearest-neighbor classical isotropic Heisenberg exchange. Proceeding from left to right, the solid curves are for rings ($N=4$, 6, 8, 10, ∞) and the dashed curves are for chains ($N=4$, 6, 8). The values of the susceptibility were obtained using Eq. (2.13a) along with Eqs. (2.14) and (2.16) for rings and chains, respectively.

$$\tilde{\chi}_N^{\text{chain}}(K)=\frac{1+u}{1-u}-\frac{2u}{N}\,\frac{1-u^N}{(1-u)^2}. \tag{2.16}$$

Obviously, by letting $N\to\infty$ in Eq. (2.16), we correctly recover Eq. (2.15). One can check that Eq. (2.16) reproduces the correct expressions for $N=1,2$, namely, $\tilde{\chi}_1^{\text{chain}}=1$ and $\tilde{\chi}_2^{\text{chain}}(K)=1+u(K)$.

Using the above formulas, we display in Figs. 1–3 the zero-field susceptibility per spin for classical Heisenberg rings and chains for both ferromagnetic and antiferromagnetic interactions. In each of these figures the susceptibility per spin is given in units of $\mu_c^2/(3|J_c|)$. In Fig. 1 results are shown for the case $J>0$. The major feature to observe is that, for both chains and rings, already for small values of N the results very nearly coincide with those for $N\to\infty$. In Fig. 2 we display results for the case $J<0$ and for *even* values of N. Note that, for the case of the rings, the results for finite N very quickly converge to that for $N\to\infty$. A very different behavior occurs for finite chains. It is noteworthy that for the chains, the dependent variable approaches unity in all cases in the low temperature limit. Note also that only for $N>1000$ have the results converged to that for $N\to\infty$, and then only if $k_BT/|J_c|$ is not too small. In Fig. 3 we demonstrate the differences between rings composed of even and odd values of N when $J<0$. Only for even values of N is there a common low-temperature limit, 0.5. For increasing odd values of N, the curves decrease monotonically towards the limiting curve for $N\to\infty$. By contrast, the curves for increasing even values of N monotonically approach the limiting curve from below. The overall behavior is in accord with the expectation that for sufficiently large values of N there cannot be any difference between an even and odd number of spins. Put differently, the low-temperature behavior for small rings consisting of an odd number of spins is dominated by frustration effects. Frustration is a predominant feature especially for $N=3$. For this system, the low-temperature limit of the correlation function turns out to be given by $\langle \hat{e}_1\cdot\hat{e}_2\rangle=-1/2$, which translates to each spin being oriented 120° with respect to its neighbors. In Ref. 13, a detailed discussion is given on frustration effects in quantum and classical Heisenberg rings, and the dependence of these effects on N and S.

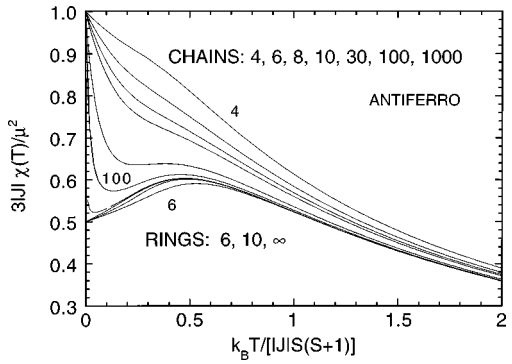

FIG. 2. Zero-field magnetic susceptibility per spin, for chains and rings consisting of an even number of spins interacting via antiferromagnetic nearest-neighbor classical isotropic Heisenberg exchange. The values of the susceptibility were obtained using Eq. (2.13a) along with Eqs. (2.14) and (2.16) for rings and chains, respectively.

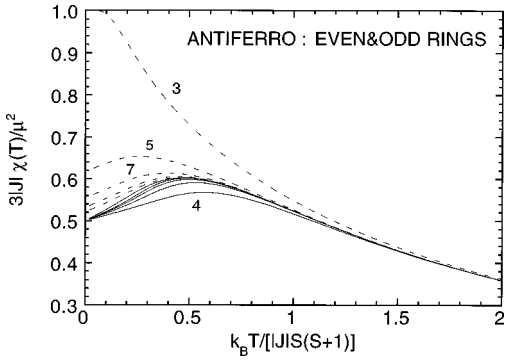

FIG. 3. Zero-field magnetic susceptibility per spin for rings consisting of an even (solid curves) and odd (dashed curves) number of spins interacting via antiferromagnetic nearest-neighbor classical isotropic Heisenberg exchange, for $N=3-11,\infty$. The values of the susceptibility were obtained using Eq. (2.13a) along with Eq. (2.14).

III. APPROXIMANTS

A. Correlation functions

In this and the following subsection we present simple approximate formulas for the two-spin correlation function $C_N(n,K)$ and the susceptibility $\chi_N(K)$ for a classical Heisenberg ring of N spins and compare these with the exact expressions (2.7) and (2.14) given in the previous section. As stated in the Introduction, we anticipate that the correlation function for a ring of spins should initially incorporate exponential decay with increasing n as well as fulfill the cyclic condition Eq. (2.3). Proceeding from a given site i to a site $i+n$ on the ring, in keeping with the exponential decay of correlations that is well known to occur for an open chain of Ising or Heisenberg spins, the spin correlation function $\langle \hat{e}_i\cdot\hat{e}_{i+n}\rangle$ should display similar decay. On the other hand, if one draws a diameter of the ring through site i, it is clear that spin i should be correlated in the same way with each of the pairs of spins that are positioned symmetrically with respect to that diameter. Both of these features are in fact exhibited by each individual term contributing to the series represen-

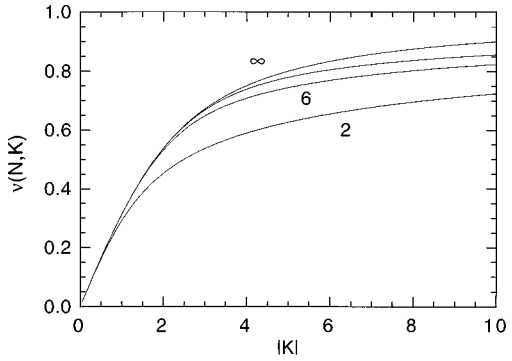

FIG. 4. The functions $\nu(N,K)$ for $N=2,6,10,\infty$ as obtained using (3.4), where $C_N(N/2,K)$ is the exact correlation function for a pair of spins at opposite ends of a diameter of a rings of N spins. The functions $\nu(2,K)$ and $\nu(\infty,K)$ are given by Eqs. (3.3) and (3.2), respectively, while $C_6(3,K)$ and $C_{10}(5,K)$ have been calculated using Eq. (2.7).

tation (2.7) of the exact correlation function. Each term of the infinite series consists of two subterms, one of which, $\rho_l^n(K)$, decays with increasing n, while the other, $\rho_l^{N-n}(K)$, grows with increasing n.

Seeking the *simplest* possible mathematical form embodying these twin requirements, we are led to approximate the correlation function by

$$C_N(n,K)=[\nu^n(N,K)+\nu^{N-n}(N,K)]/[1+\nu^N(N,K)], \tag{3.1}$$

where $\nu(N,K)$ is some appropriately chosen function of the coupling constant K and N. Without any loss of generality we may suppose that the magnitude of $\nu(N,K)$ is less than unity, since the right-hand side of Eq. (3.1) is invariant under the substitution $\nu(N,K)\rightarrow 1/\nu(N,K)$. We note that Eq. (3.1) preserves the identity $C_N(0,K)=1$. In order to meet the large-system limit, Eq. (2.8), we must have

$$\lim_{N\rightarrow\infty}\ \nu(N,K)=u(K), \tag{3.2}$$

where $u(K)$ is the Langevin function, Eq. (2.9). This suggests that the simplest version of Eq. (3.1) would consist of adopting the choice $\nu(N,K)=u(K)$ for sufficiently large N. In fact, as shown below, the resulting approximate correlation function performs very well for $N\geqslant 6$ as long as $|K|<3$, i.e., for sufficiently high temperatures. We adopt this approach in the following subsection as well as in Sec. IV, where we find that we can accurately reproduce the experimental data for the zero-field susceptibility of the molecular ferric wheel ($N=10$) for temperatures above 50 K. On the other hand, the selection for $\nu(N,K)$ must surely depend on N for sufficiently small values of N. This is most readily demonstrated for $N=2$. Suppose that we choose the function $\nu(2,K)$ by requiring that Eq. (3.1), for $N=2$ and $n=1$, coincide with the exact result $C_2(1,K)=u(2K)$. In this case one finds that

$$\nu(2,K)=\frac{1-\sqrt{1-u^2(2K)}}{u(2K)}. \tag{3.3}$$

In Fig. 4, the curves labeled 2 and ∞ correspond, respectively, to $\nu(2,K)$, given by Eq. (3.3), and $u(K)$, as functions of K.

TABLE I. Correlation functions $C_N(n,K)$ for $N=6$. For each value of K the entries of the first row are obtained using the approximation (3.1), where $v(6,K)$ is chosen according to Eq. (3.4). The entries of the second row are calculated using the exact series expansion (2.7).

K	$C_6(1,K)$	$C_6(2,K)$	$C_6(3,K)$
1	0.315589	0.107381	
	0.315517	0.107364	0.06120426
2	0.561149	0.354165	
	0.559293	0.353548	0.2935233
10	0.916467	0.867577	
	0.915634	0.867250	0.851484

An improved procedure for selecting the form of $\nu(N,K)$, as compared to using $\nu(N,K)=u(K)$ for all N, then consists of the following. We limit our attention to even values of N and require that our approximate formula, Eq. (3.1), coincide with the exact values of $C_N(N/2,K)$, as computed from Eq. (2.7), for all values of K. Imposing this requirement provides a quadratic equation for the quantity $[\nu(N,K)]^{N/2}$ and thereby fixes the form of $\nu(N,K)$ as

$$\nu(N,K)=\left[\frac{1-\sqrt{1-[C_N(N/2,K)]^2}}{C_N(N/2,K)}\right]^{2/N}. \tag{3.4}$$

[Note that this formula includes the result Eq. (3.3) for $\nu(2,K)$ as a special case.] We then compare the predictions of Eq. (3.1) with those of the exact formula, Eq. (2.7), for $n=1,\ldots,(N/2)-1$, using the choice Eq. (3.4) for $\nu(N,K)$. Using Eq. (3.4) for $N=6,10$ leads to the curves shown in Fig. 4 along with the exact functions $\nu(2,K)$ and $\nu(\infty,K)$. The most striking feature of this plot is that except for low temperatures ($|K|>3$) there is very little difference between the three functions $\nu(6,K)$, $\nu(10,K)$, and $\nu(\infty,K)$. That is, the crudest approximation, of adopting the quantity $\nu(\infty,K)=u(K)$ for $\nu(N,K)$, performs very well for all $N\geqslant 6$ in the temperature range $|K|<3$. Of course, the larger the value of N, the larger temperature range over which this approximation is successful.

We now examine the error that arises in using Eq. (3.1) in conjunction with Eq. (3.4) to approximate the exact correlation function. In Tables I and II we list exact as well as approximate values of $C_6(n,K)$ for $n=1,2,3$ and $C_{10}(n,K)$ for $n=1,\ldots,5$ for the relatively low temperature $|K|=10$ as well as for $|K|=1,2$. The agreement is excellent and improves significantly as one considers higher temperatures. We have not discussed the quality of the fit provided by Eq. (3.1) for $|K|>10$ since the replacement of the underlying quantum Heisenberg model, Eq. (2.1), by the classical Heisenberg model, Eq. (2.1′), must be invalid at sufficiently low temperatures. The purpose of using Eq. (3.4) is to explore in principle to what extent is the n-dependence of the correlation function satisfactorily described by the functional form Eq. (3.1). We have just seen that this approach does indeed provide a very accurate fit to the exact values of $C_N(n,K)$. However, for practical work, for $N\geqslant 6$ one can

TABLE II. Correlation functions $C_N(n,K)$ for $N=10$. For each value of K the entries of the first row are obtained using the approximation (3.1), where $v(10,K)$ is chosen according to Eq. (3.4). The entries of the second row are calculated using the exact series expansion (2.7).

K	$C_{10}(1,K)$	$C_{10}(2,K)$	$C_{10}(3,K)$	$C_{10}(4,K)$	$C_{10}(5,K)$
1	0.313034	9.80818×10^{-2}	3.09686×10^{-2}	1.05430×10^{-2}	
	0.313059	9.80813×10^{-2}	3.09685×10^{-2}	1.05429×10^{-2}	6.01154×10^{-3}
2	0.539578	0.294630	0.167339	0.106873	
	0.539252	0.294407	0.167242	0.106850	8.90855×10^{-2}
10	0.910611	0.843233	0.796236	0.768485	
	0.908610	0.841284	0.795120	0.768170	0.759308

skirt the task of computing $C_N(N/2,K)$ which is needed in Eq. (3.4), and instead use Eq. (3.1) in conjunction with the simplified choice $\nu(N,K)\to u(K)$.

B. Susceptibility

We now calculate the zero-field susceptibility using the approximate correlation function (3.1) for the simplest choice $\nu(N,K)=u(K)$. Simple algebra yields the following result for the reduced susceptibility $\tilde{\chi}_N(K)$ of Eq. (2.13b):

$$\tilde{\chi}_N(K)=\frac{[1+u(K)][1-u^N(K)]}{[1-u(K)][1+u^N(K)]}. \tag{3.5}$$

In the following section we compare exact numerical values of $\tilde{\chi}_N(K)$, obtained using Eq. (2.14), with those obtained using Eq. (3.5). Both sets of results are also compared to experimental data for the ferric wheel molecular cluster. We remark that Eq. (3.5), rewritten as $\chi_N/\chi_\infty=(1-u^N)/(1+u^N)=\tanh[N/(2\xi)]$, gives a simple expression for the finite-size scaling function for the susceptibility.

IV. COMPARISON WITH EXPERIMENT

The molecular ferric wheel ($[Fe(OCH_3)_2(O_2CCH_2Cl)]_{10}$) is one of a variety of polynuclear metal complexes that have been synthesized[3,4] in recent years. Prepared as powder samples, the individual molecules appear to make independent contributions to the magnetic susceptibility, i.e., the intercluster magnetic interactions are thought to be negligible. The source of the magnetic properties of a given molecule are the ten paramagnetic Fe^{3+} ions uniformly spaced along a ring-shaped structure. The spin angular momentum of an Fe^{3+} ion is $S=5/2$, its orbital angular momentum is quenched, and thus the value of the g factor is $g=2$. It has been established[4] that these ten ions interact with nearest-neighbor antiferromagnetic isotropic Heisenberg spin exchange. That is, the magnetic properties can be described in terms of the Hamiltonian (2.1), where the exchange interaction energy (in units of k_B) has been estimated[4] to be approximately $J=-14$ K. In the corresponding classical Heisenberg model, Eq. (2.1′), the associated values of the interaction parameters are $J_c\approx-122.5$ K and $\mu_c=-\sqrt{35}\mu_B$, respectively. It should be noted that the assignment of the above numerical value of J was made in Ref. 4 by comparing experimental susceptibility data to the predictions of two theoretical models. The first was the classical Heisenberg model, (2.1′), for an *infinite* chain of spins, and the second was a quantum-mechanical calculation performed for an 8-spin ring described by the (quantum) Heisenberg model (2.1).

In Fig. 5 we show unpublished experimental molar susceptibility data (+ symbols) which were obtained[8] at Universitá di Firenze for a powder sample in a 1 T magnetic field. This data agrees quite well with that reported in Ref. 4 for 0.3 T. We estimate that the peak value, 0.2072 emu/mol, occurs at the temperature $T=60$ K. We then required that the exact theoretical formula for the molar susceptibility, starting from the zero-field expressions (2.13a) and (2.14), also have its peak at this temperature. This requirement is met upon adopting the value $J\approx-14.114$ K, which is very close to the previous[4] estimate. In Fig. 5 the solid curve is the prediction of the exact theory for the molar susceptibility, multiplied by an overall constant, 0.9728, so as to pin the peak theoretical value at the peak measured value, 0.2072 emu/mol. [The molar susceptibility is obtained by multiplying Eq. (2.13a), the susceptibility per spin, by $10N_A$, where N_A is Avogadro's number, since each cluster contains ten magnetic ions.] Thus, we find that the theoretical value for the molar susceptibility is 2.8% larger than the corresponding experimental value. We believe that this agreement is quite satisfactory given the fact that the experimental data is affected

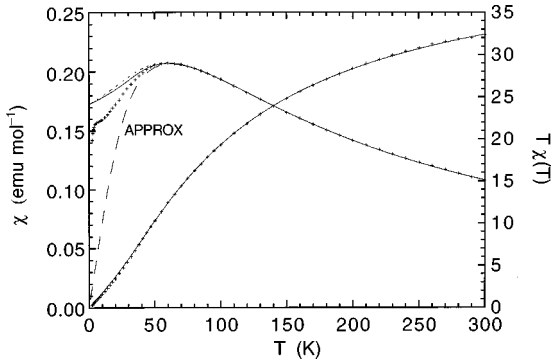

FIG. 5. Molar susceptibility (experimental and classical Heisenberg systems) versus temperature for the ferric wheel molecular cluster: Experimental data for a magnetic field of 1 T (+); exact theory, ring, (solid curve); approximate theory, ring (long dashes); exact theory, infinite chain (short dashes). Also shown are values of $T\chi(T)$. This quantity will approach a constant limiting value, ≈43 emu K/mol, in the high-temperature regime (Curie's law). As explained in Sec. IV, each of the theoretical expressions for the molar susceptibility has been multiplied by a numerical factor of 0.9728 in order that the peak of the solid curve equals that of the experimental data (0.2072 emu/mol).

by the external magnetic field and it has been assumed that the powder sample was composed of identical molecules. Put differently, this level of agreement between theory and experiment affirms the high degree of purity of the experimental powder sample, pictured as identical, unblemished ferric wheels each incorporating ten Fe^{3+} ions.

Also shown in Fig. 5 are the approximate molar susceptibilities derived from Eq. (3.5) (long dashes), and from the infinite-chain classical Heisenberg antiferromagnet (short dashes), i.e., proportional to $(1+u)/[T(1-u)]$. All of the theoretical formulas are for the zero-field molar susceptibility and each has been multiplied by the same overall multiplicative constant given above. The close agreement between the infinite chain susceptibility and the approximate susceptibility (3.5) is to be expected since these two quantities differ by terms of order u^8, and even for such a low temperature as $T=50\,\mathrm{K}$ we have $u^8 \approx 0.02$. For increasing temperatures this difference rapidly decreases to zero. What could not be anticipated, however, without evaluating Eq. (2.14), is the close agreement between the exact susceptibility of the finite Heisenberg ring and the approximate susceptibility, Eq. (3.5). Furthermore, inspecting Fig. 5 one sees that below approximately 40 K, the molecular ferric wheel susceptibility cannot be accurately described by the classical Heisenberg model. For this system, therefore, there is no advantage to the exact susceptibility (2.14) over the simple, approximate form (3.5).

We have also included in Fig. 5 the values of the quantity $T\chi(T)$. At sufficiently high temperatures this quantity, per mole, must approach a constant limiting value (Curie's law), given by approximately 43 emu K/mol. More specifically, in the high-temperature regime one can ignore all of the functions $f_l(K)$ in Eqs. (2.5) and (2.14), since for small values of K one has [see Eq. (10.2.5) of Ref. 17] $f_l(K) = O(K^n)$, except for $f_0(K) \approx 1$. It is then straightforward to derive the first two terms of the high-temperature expansion of the molar susceptibility, in powers of $|J|/(k_B T)$, as

$$T\chi \rightarrow N_A (g\mu_B)^2 \frac{S(S+1)}{3k_B}\left[1 - \frac{\theta}{T} + O(1/T^2)\right], \qquad (4.1)$$

where $\theta \equiv 2|J|S(S+1)/(3k_B) \approx 82.33\,\mathrm{K}$ is known as the paramagnetic Curie temperature. The excellent fit between experiment and the exact formula for $T\chi(T)$ even at very low temperatures is of course due to the factor T which minimizes the differences in $\chi(T)$. Nevertheless, if nothing else, the excellent fit over the entire temperature range shown emphasizes that an isotropic nearest-neighbor Heisenberg model of spins on a finite ring provides an excellent framework for explaining the magnetic properties of the ferric wheel. It is remarkable that a synthesized material should adhere so closely to the model.

V. DISCUSSION

This article has had two purposes. First, we have demonstrated (see Fig. 5) that a classical treatment of Heisenberg spins situated on a small ring leads to results in excellent agreement with the measured magnetic susceptibility of the ferric wheel molecular cluster for all but low temperatures. The classical approximation consists of replacing the quantum spin operators with vectors of length $\sqrt{S(S+1)}$ that are free to point in any direction. For the Fe^{3+} spins of the ferric wheel, $S=\frac{5}{2}$. As discussed in Sec. IV, we have fit the computed results to the experimental data, first by adjusting the exchange constant J so that the temperature associated with the peak in the computed susceptibility agreed with that for experiment, and second, by adjusting an overall multiplicative constant so that the value of the theoretical susceptibility coincided with experiment at one temperature, that of the peak. The resulting value of J is quite close to previous[4] estimates, obtained with other models. Furthermore, for temperatures above that of the peak, the theoretical susceptibility is in excellent agreement with the measured values. We note, however, that even without making the peak values agree using an adjustable parameter, our absolute determination of the molar susceptibility agrees with experiment to within 3%. We believe this amply confirms the utility of the classical approximation to predict the susceptibility for all but low temperatures. We reiterate, we also believe that this level of agreement affirms the high degree of purity of the experimental sample, pictured as identical, unblemished ferric wheels.

The second purpose of this article was to demonstrate the remarkable efficacy of the approximation (3.1) to the two-spin correlation function. We approximated the exact correlation function, given by Eq. (2.7), by a sum of two terms: The first term implies exponential decay for $C_N(n)$ for $|n| \ll N$, whereas the second term ensures that the cyclic property given by Eq. (2.3), $C_N(n) = C_N(N-n)$, is obeyed. We then used the approximate correlation function to obtain an associated approximant for the zero-field susceptibility, Eq. (3.5). The form listed for Eq. (3.5) is given in terms of the Langevin function, $u(K)$, which is related to the exact correlation length, ξ, by $|u| = \exp(-\xi^{-1})$. As we have seen, this approximation gives results for the susceptibility in excellent agreement with the exact quantity for all but very low temperatures. As discussed in Sec. III, Eq. (3.5) represents the susceptibility upon using the simplest choice of the function $\nu(N,K)$ in Eq. (3.1), namely its large-N limiting form, Eq. (3.2), which turns out to be $u(K)$. A greatly improved choice is provided by Eq. (3.4). However, in view of the excellent agreement for the susceptibility already achieved using Eq. (3.2), it seems pointless to invoke the ultra-high accuracy offered by Eq. (3.4).

In short, we have shown that classical Heisenberg spins can approximate extremely well the observed magnetic behavior of small quantum Heisenberg rings. We have also shown that, instead of employing the complicated machinery of Joyce's exact solution to the classical Heisenberg ring, one can obtain results of high accuracy making use of the extremely simple approximants discussed in this article. Hopefully this will simplify the task of comparing experimental data with the predictions of the classical Heisenberg model. More generally, we hope that as molecular magnetic systems continue to be explored for their possible applications, the approximants discussed here will prove useful in accelerating the development of a nanomagnetic technology.

ACKNOWLEDGMENTS

We thank A. Lascialfari and D. Gatteschi for sending us their unpublished susceptibility data for ferric wheels. We also thank P. Canfield and D. C. Johnston for useful comments. Ames Laboratory is operated for the U.S. Department of Energy by Iowa State University under Contract No. W-7405-Eng-82.

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